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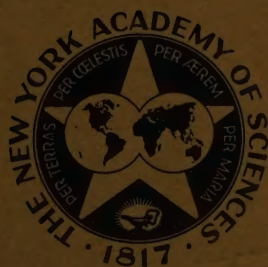
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FRANKLIN N. FURNESS

DETERMINATION OF SR^{90} AND BA^{140} IN BONE,
DAIRY PRODUCTS, VEGETATION, AND SOIL

By

H. L. VOLCHOK, J. L. KULP, W. R. ECKELMANN, AND J. E. GAETJEN



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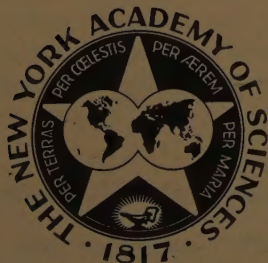
Isotopes Incorporated, Westwood, N.J.

J. L. KULP, W. R. ECKELMANN

Lamont Geological Observatory (Columbia University), Palisades, N.Y.

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Introduction

Fission product contamination in many natural materials requires an efficient chemical procedure for the separation, purification, and absolute measurement of certain isotopes at very low levels. As part of the study of the distribution of long-range fall-out from nuclear tests, a technique for the determination of both strontium-90 and barium-140 has been developed. The sample materials include bone, cheese, milk, vegetation, and soil. The first four sample types contain calcium phosphate as a major part of their ash. The separation of the phosphate from calcium, strontium, and barium is necessary for these sample types. Soils contain exchangeable calcium as well as nonexchangeable calcium in the silicate lattices. Since strontium and barium will follow calcium under the proper conditions, procedures were designed around the chemistry of calcium, which acts as a carrier for strontium and barium. In all cases the preliminary chemical procedure yields a calcium chloride solution carrying the radioactive strontium and barium. The radioactivity measurements are made on the daughters of strontium-90 and barium-140, that is, yttrium-90 and lanthanum-140, respectively, which are extracted from the solution.

Preliminary Chemical Procedures

Bone, cheese, milk, and vegetation. The main objective of this phase of the procedure is to obtain a pure solution containing the mother

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radio-element (Sr^{90} and Ba^{140}) which is in a form suitable for "milking," that is, the quantitative extraction of the daughter. The separation of the daughter (Y^{90} , La^{140}) from the mother (Sr^{90} , Ba^{140}) is rather difficult in solutions containing phosphate ion, since the phosphates of the two groups precipitate in a very narrow pH range. Alkaline earth phosphates precipitate at a pH of about 2.4, while rare earth phosphates come down at about 1.5. In this procedure pH control is difficult, since the solution is hot and the ammonia content varies with time and temperature. For these reasons it is desirable to separate the phosphate ion from the alkaline earths.

Samples of all of these materials are first completely ashed at about 600°C . The ash containing the strontium and barium in calcium phosphate is then taken up in an excess of concentrated hydrochloric acid and the solution filtered to remove insolubles.

In order to separate the phosphate ion, ammonium hydroxide is added to the clear filtrate to bring the pH to 1.5, after which ammonium oxalate is added in excess. The calcium oxalate forms, carrying with it the strontium and barium quantitatively, leaving the phosphate ion in solution. The calcium oxalate is filtered and ignited to calcium oxide at 600°C . The completeness of removal of the phosphate is tested by dissolving the calcium oxide in hydrochloric acid and raising the pH above 3.0. Formation of a precipitate indicates that appreciable phosphate was carried down in the oxalate precipitation. If such a precipitate forms, the pH is lowered to 1.0 again (dissolving all of the phosphate) and the oxalate precipitation is repeated. Once the calcium chloride solution is found free of phosphate, the preparation of the mother solution is complete, and it may be milked repeatedly for Y^{90} and La^{140} without loss of Sr^{90} and Ba^{140} .

Soil. The exchangeable calcium, Sr^{90} and Ba^{140} , in soil may be removed by two leaching procedures:

- (1) A 1000-gm. aliquot of the original sample of soil is mixed with 4 liters of a 1 N ammonium acetate solution and allowed to stand for 24 hr. The sample is then filtered and washed with 500 ml. of 1 N ammonium acetate and the filtrate evaporated to dryness. The residue is dissolved in 6 N HCl and the calcium is precipitated as the oxalate at a pH of 1 to 1.5.

- (2) Two liters of 6 N HCl are added to a 1000-gm. aliquot of the soil sample and allowed to stand for 24 hr. The mixture is then filtered and washed with 250 cc. of 6 N HCl. The filtrate is evaporated to dry-

ness and ashed at 600°C . for 15 hr. The residue is dissolved in 6 N HCl and sufficient hydrogen peroxide is added to convert ferrous to ferric iron. The pH is then raised to 7.5 by the addition of NH_4OH and the hydrous ferric oxide filtered off. This solid is dissolved and reprecipitated under the same conditions previously described. The filtrates are then combined, and the calcium is precipitated as the oxalate.

The portion of the Sr^{90} or Ba^{140} in a form insoluble in NH_4Ac or HCl is obtained by fusing about 160 gm. of Na_2CO_3 with 40 gm. of soil, followed successively by solution in water and 3 N HCl. After the siliceous residue is filtered off, the alkaline earth is precipitated. No appreciable Sr^{90} activity remains in this siliceous residue, as may be proved by dissolving several samples of this siliceous residue completely and then carrying out radiometric assay.

In all cases the oxalate is reprecipitated and then ignited to the oxide and weighed in order to determine the calcium content. The oxide is then dissolved in dilute HCl, producing the mother solution.

Milking Procedure

The milking of the mother solution for the daughter isotopes is essentially a two-step process designed (1) to separate the yttrium and lanthanum daughters quantitatively from the alkaline earth mothers, and (2) to produce a precipitate of the daughters suitable for radioactivity measurement. Separation is accomplished simply by raising the pH of the mother solution to about 5 with ammonium hydroxide after adding about 10 mg. of nonradioactive yttrium carrier. A white gelatinous precipitate of yttrium hydroxide (carrying with it the yttrium-90, lanthanum-140, and the rare earths) will quickly form and coagulate satisfactorily if heated for a few minutes. This precipitate is filtered, the time of precipitation is recorded, and the filtrate is stored for later milkings when the daughters have again appeared. Other long-lived rare earth fission products and natural radioactive isotopes that are carried with the alkaline earth oxalate precipitation are separated in this first milking. A second milking of the mother solution is generally required to obtain only yttrium-90 or lanthanum-140.

The gelatinous nature of the hydroxide precipitate makes it unsatisfactory for counting. Therefore, it is dissolved off the filter paper with 6N hydrochloric acid, the pH is adjusted to the point just below precipitation, and excess oxalic acid is added. This precipitates yttrium oxalate, an ideal solid for measurement of radioactivity because of its coarse

granularity. The precipitate is filtered on a stainless steel funnel with suction and dried by pulling air through the sample for about ten minutes. The filter paper with the sample is then removed, mounted for counting on a brass disk, covered with Pliofilm, and secured with a brass ring.

Yttrium carrier completely free of natural radioactivity is very difficult to obtain. After trying several sources, reasonably good yttrium oxide was obtained from A.D. MacKay Co., New York, N.Y. The oxide is purified further by dissolving it in HCl, precipitating it as the hydroxide, converting it to the oxalate, and igniting it to the oxide. Once the yttrium carrier is pure it may be reused repeatedly for successive milkings. Carrier used for first milkings is saved and repurified. It is convenient to use unselected C.P. Yttrium oxide from any source for first milkings of soil and vegetation samples, since they are normally discarded. On the other hand, the bone and milk samples are often so free from natural or artificial contamination that the first milking can give a reliable assay. In this case, of course, the nonradioactive carrier must be used.

Radioactive Procedure

The radiometric determination of the final precipitate is done in a specially designed beta counter¹ that utilizes anticoincidence shielding to obtain low background.

The relatively short half lives of the daughter products, $64.24 \pm .30$ hours for yttrium-90 and 40 hours for lanthanum-140, make it desirable to count these isotopes rather than the parent isotopes strontium-90 (19.9 years) and barium-140 (12.8 days) for two reasons: (1) the decay of the daughter isotopes may be followed to detect contamination; and (2) repeated milkings from the same mother may be made after only a few days.

In the case of samples several months old only Sr^{90} is detected. If the Ba^{140} and Sr^{90} are present in similar but high concentrations, they may be conveniently analyzed together, either by a detailed analysis of the mixed daughter decay curve or by milking a third time 2 weeks later. In the case of similar but very low level activities of both Sr^{90} and Ba^{140} it is desirable to pass the CaCl_2 solution through an ion exchange column after adding nonradioactive strontium and barium carriers to effect the separation of the Ba^{140} and Sr^{90} prior to milking. The apparatus consists of a 2.2×20 cm. column of 200 to 400 mesh Dowex-50 cation exchange resin (8 per cent cross linkage). The sample is placed on the column as the chloride, and the column is eluted with 4 N HCl at a rate of approximately 0.3 ml./min. Approximately 5 1/2 hours are required to

complete a collection. Calibration was carried out with radioactive strontium, yttrium, barium, and lanthanum. Stable calcium was determined spectrometrically. Under the prescribed condition no traces of calcium (peak at 192 ml.), strontium (peak at 25⁶ ml.), and yttrium (peak at 288 ml.) remain at the onset of barium elution. Barium peaked at 672 ml. and therefore only two collections need be made: the first from the first drop of eluant to 480 ml., and the second from 481 ml. to 832 ml. After this separation the two solutions are milked as described above.

Results

Over one hundred samples have been run by this method. To evaluate the absolute accuracy of this procedure the several steps will be discussed separately.

Recovery of calcium. The completeness of the conversion of calcium phosphate to calcium oxalate was defined by gravimetric analysis of pure calcium phosphate samples. It was found that more than 98 per cent of the calcium originally present as phosphate is recovered as calcium oxalate.

Recovery of strontium. A radioactive spike of strontium-90 was added to a solution of "dead" calcium phosphate, which was precipitated as phosphate and filtered. This precipitate was then taken through the procedure described above. The results showed that at least 98 per cent of the carrier-free strontium was recovered. Repeat milkings showed no evidence of measurable loss of strontium from the mother solution.

Efficiency of separation in milking. A series of samples was prepared using spikes of radioactive strontium. These samples gave count rates between 800 and 1300 counts per minute. The half life of yttrium-90 was derived by observing the decay of the mounted samples.² Counting the samples after more than six half lives of yttrium-90 have elapsed indicated that the separation of yttrium-90 from strontium-90 in the milking is quantitative. TABLE 1 lists the data for this experiment.

Reproducibility. Many of the samples have been milked two or more times. TABLE 2 lists the data on several of these natural samples, indicating the degree of precision obtained by this method.

Soil extraction. It was necessary at the outset of the program to establish the reproducibility of the extraction of "available calcium and Sr^{90} ." TABLE 3 shows that aliquots of the same soil give an average deviation of approximately 1 per cent on duplicate runs.

Although the leaching procedure is fairly reproducible, one ammonium acetate treatment does not remove all of the Sr^{90} that is present (TABLE 4). Several samples from the New York, N.Y., area were leached two or three times. Each set showed a successive decrease of the Sr^{90}/Ca ratio, indicating that the Sr^{90} is more readily available than the calcium, and that at least 80 per cent comes out in the first leach.

TABLE 1
EFFICIENCY OF SEPARATION OF Sr^{90} AND Y^{90} IN MILKING

Sample No.	Initial cpm (Immediately after milking)	Final cpm (After more than 6 half lives)
HC-97	1087±15	0.03
HC-99	1171±20	0.03
HC-100	940±10	0.01
HC-101	1010±10	0.02
HP-100	1220±10	0.03
HP-101	860±9	0.02
HP-102	1000±10	0.01
HP-103	1260±11	0.01

TABLE 2
PRECISION DETERMINED BY REPEATED
MILKINGS

Sample No.	Milk No.	Sr^{90} content (arbitrary units)
B-3	2	1.43±0.08
	3	1.44±0.08
B-16	1	0.20±0.04
	2	0.15±0.05
C-6	2	0.97±0.07
	3	1.14±0.05
C-10	1	0.85±0.09
	2	0.77±0.10

A sample of soil from the same vicinity as that used for the NH_4Ac treatment was leached with 6 N HCl. A single treatment removed 99 per cent of the leachable activity, and the second and third leaches removed calcium in successively smaller quantities (TABLE 4). Finally, the leached soil was fused with Na_2CO_3 to determine the Sr^{90} in nonex-

changeable form. Apparently this contributes about 40 per cent of the total in this sample.

It is concluded that the experimental procedures for low level measurement of Sr⁹⁰ and Ba¹⁴⁰ in this variety of materials give satisfactory results.

TABLE 3
REPRODUCIBILITY OF CALCIUM EXTRACTIONS
(NH₄ AC METHOD)

Sample No.	Sample size (grams)	Ca (gm.) extracted
17A	1000	0.0612
A'	1000	0.0606
16A	1000	1.952
A'	1000	2.020
37A	1000	0.0936
A'	1000	0.0912

TABLE 4
EFFECT OF SUCCESSIVE NH₄AC AND HCl LEACHES OF SOIL
SAMPLES FROM PALISADES, N. Y.

Sample No.	Method	Leach	Ca (gm.)	Cpm	Cpm/ Ca
S-1	NH ₄ Ac	1st	3.97	35.5±.2	8.94
S-1		2nd	1.69	6.21±.02	3.67
S-1		3rd	0.55	1.32±.18	2.40
S-4	HCl	1st	2.06	164 ± 6	—
S-4		2nd	0.89	≤.8	—
S-4		3rd	0.45	≤.6	—
S-4		fusion	—	110 ± 10	—

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1. VOLCHOK, H. L. & J. L. KULP. 1955. A low-level beta counter for routine radiochemical measurements. *Nucleonics*. 13(8): 49-50.
2. VOLCHOK, H. L. & J. L. KULP. 1955. Half-life of yttrium-90. *Phys. Rev.* 97: 102.

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